SILVER-CADMIUM BATTERY DEVELOPMENT PROGRAM

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THIRD QUARTER, ENDING 20 May 1962

DATED

2 August 1962

CONTRACT NO. NAS5-1431

POWER SOURCES DIVISION
Telecomputing Corporation

Prepared by:

J. W. Rhyne

John W. Rhyne
Chief Electrochemist

Approved by:

S. Groner
M.C.C.

S. Groner
Director of Engineering

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John Rhyne, Jr.

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CONFERENCES

A conference was held at Goddard Space Flight Center, NASA, Greenbelt, Maryland, on May 25, 1962.

Those present were:

NASA - Mr. P. C. Donnelly
Mr. T. J. Hennigan

Telecomputing Corporation - Mr. J. Winther
Mr. J. W. Rhyne

The current status of the program was discussed. This included problem areas encountered and the progress made toward successful conclusion of the project. The following items were delivered to the NASA personnel:

1. Two multi-plate test cells, hand fabricated containers.

2. Sample molded case.

3. Two dummy bipolar battery monoblocks.

4. Glass filament wound outer case.

A conference was held at Power Sources, Denver, Colorado, on March 14, 1962.

Those present were:

Narmco R & D - Mr. S. E. Susman
Mr. B. Levenetz

Power Sources - Mr. J. W. Rhyne
Mr. S. Groner
Mr. J. Essex

REPORT

PHASE I - CONTAINER DESIGN AND DEVELOPMENT

Due to the change in basic cell design, reported in the Second Quarterly Report, it was necessary to investigate the suitability of various materials for the individual cell case. This work was done under sub-contract to Narmco Research and Development as part of their activities on this phase.

Cell Case

A literature survey of the properties of various plastic materials was made. Aside from the stability to concentrated alkali solutions, the water permeability was considered to be of prime importance. Unfortunately, all of the potential molding resins have not been evaluated, or at least data concerning water permeability has not been reported. Most of the available information is for film materials, such as would be used in packaging, etc. Nevertheless, the data which is available suggests definite trends by which the selection of a workable material for the cell case can be made. A tabulated summary of the permeability data is given in Table 1. The various materials are rated in terms of water vapor, oxygen, and nitrogen permeabilities.

Consideration of the chemical structures of the various materials and the above data suggests certain relationships which might exist.

1. Hydrophobic materials, such as polyethylene, teflon, Kel-F, etc., have a low water permeability.

2. Hydrophilic polymers, such as Mylar, nylon, and polymethylmethacrylate are generally more permeable than the polymers classified as hydrophobic.

3. Density and molecular weight affect the permeability trend. The low density and molecular weight of polyethylene and polystyrene cause a higher permeability than would be expected from chemical considerations. *

Since all of the polymers tabulated, except mylar (a polyester), are reported to be resistant to strong KOH solutions, the selection of a suitable resin for

* The high molecular weight of nylon and mylar as well as the associated hydrogen-bond linkages appear to make these polymers intermediate to the best and poorest hydrocarbon polymers.

cell case use may be made on the basis of comparative low water permeability, moldability, bondability, and cost. It further appears to be desirable to add epoxy resins to the list of those materials to be considered. Although no specific data was found during the survey for this class of compounds it would be expected that the permeability properties to be similar to those of nylon considering chemical and other physical properties of the epoxy systems.

All of the listed resins can be molded with the exception of Teflon TFE. Only the epoxy, polystyrene and polymethyl methocryate systems can be used for cast moldings. Since the possibility of bubble occlusion or voids is high in a casting process, the resultant productive difficulties would probably out-weigh any mold cost savings. Thus with the acceptance of a molding process as the method for forming the cell case, the only considerations other than permeability are bondability and cost. Based on consideration of these factors, both the halo-carbon and nylon have definite disadvantages in these areas. Neglecting these two types from immediate consideration, Saran (polyvinylidene chloride) and epoxy systems remain. Although epoxy molding system would have better thermal properties and bondability than Saran, the Saran would be serviceable to 160°F and may be bonded with epoxy-polyamide resins or may be solvent welded. Furthermore, it has excellent water permeability characteristics as well as the lowest gas permeability of any known plastic material. This latter characteristic might well be important in the operation of the sealed battery in space.

In order to obtain more accurate information regarding the chemical resistance of Saran to the conditions which would be present in a cell, tests were conducted with samples exposed to 40% KOH and certain oxidizing agents. Samples were placed in the KOH solution and exposed to temperatures of 120° and 160°F. At both temperatures darkening of the plastic was observed, within 24 hours at 160°F and within seven days at 120°F. The presence of chloride ion was detected in the KOH solution increasing concentration as the test progressed. The presence of an oxidizing agent (H_2O_2) in other tests accelerated the effect. Thus, it appears that this type of compound does not have the required degree of chemical stability necessary for use as a secondary cell case.

At present, water permeability tests are being conducted on the polyamide-epoxy system and investigation of the possibility of a composite case being made using a chemical resistant inner material (such as styrene or epoxy) with outer layers of Saran as a moisture barrier.

Container Fabrication

In order to better evaluate possible cell container materials and to furnish cases for electrochemical evaluation of internal cell construction, a cell case mold has been developed and fabricated. The cell container and cover are shown in Figures 1 and 2. The mold, together with a molded specimen is shown in Figure 3. This mold is adaptable to the use of a variety of molding materials with minor modification.

Case Development

Three additional prototype cases have been wound and tested during this period.

Case No. 7 was wound with standard fiber but with a more elastic resin, consisting of 50% Epon 820 and 50% Lancast A. The helix angle was 52% and the density of reinforcements 30 ends per inch. After cure, the case was tested with Freon gas leak detector as well as with water with the following results:

1. Minute leakage was detectable at 3 psi Freon pressure.
2. Same spots, plus some additional, leaked at 20 psi water pressure, but pressure could be increased to 150 psi in spite of leakage.
3. A gel-coat of identical resin was slush cast inside the case, cured, and the case was tested again.
4. Leakage began to develop at 150 psi.
5. Helical fibers failed at 275 psi.
6. No detectable cracks have developed in this resin in spite of high pressure.

This test proved that the elastic resin was superior to the previously used rigid system, but that the thin composite shell was not capable of holding the required pressure without leakage. It was, therefore, decided to introduce a film as a leak barrier.

Case No. 8 was wound with DuPont Teflon FEP film and with two silver-leads between the fiberglass layers. After curing and removing the mandrel, it was tested with Freon as well as with water with the following results:

1. No leakage was detectable at a Freon pressure of 20 psi.

2. At 150 psi water pressure, some spots at the end plate joints began to leak No leakage in the cylindrical portion of the case or around the leads occured.

3. Subsequent test with Freon at 65 psi indicated that the rate of leakage in these spots was between 0 4 and 5 0 ounces per year.

4. The total weight of the case (shell and end plates) was 0.27 pounds.

This test proved that the Teflon film is an effective leakage barrier and shall be recommended for future cases instead of the gel-coat. It proved also that an improvement of the structure at the end plate joint is necessary. It is believed that the main reason for leakage in this area is the non-uniform fiber distribution due to slippage of the fibers during the winding operation.

Case No. 9 was wound with redesigned end plates. This new configuration proved to be effective in reducing fiber slippage. This case has been subjected to the following tests:

1. Hydrostatic test at 150 psi.
   No leakage was detectable after five minutes at this pressure.

2. Freon gas test at 50 psi
   No leakage detectable

3. Freon gas test up to 150 psi
   Up to 140 psi no leakage was detectable During pressure increase to 150 psi leakage occurred at a rate of approximately five ounces per year. The leak at one spot at the end plate joint opposite the fill fitting.

4. Hydrostatic test to burst.
   At 150 psi slow formation of water drops appeared at the spot of leakage detected under item 3, but pressure could be increased up to 310 psi without more leakage. At this pressure the fitting end of the case failed in longitudinal tension.

Figure 4 shows this case after test. The shape of the end plates should be noted.

Inspection revealed that the Teflon liner of the case had formed blisters which were filled with Freon gas. It was concluded that Freon had penetrated the Teflon film during the pressure testing This, however, apparently had no effect on the integrity of the case Freon gas is only a medium for testing and is not present in the actual battery.

PHASE II - ELECTROCHEMICAL DESIGN

Based on the design outlined in the Second Quarterly Progress Report two cells (G and H) were constructed using fabricated cell cases having internal dimensions comparible with those shown for the molded case in Figure 1. These cases were machined from acrylic tubing and sheet. The cells were fitted with conventional terminals to facilitate individual cell testing.

These cells consisted of eleven plates, five positives and six negatives with each plate heat sealed in absorbant non-woven dynel separator. Four layers of cellophane were used for the membrane separator material. Further details of plate and cell construction are as follows:

1. Positive Plate: Resin bonded silver powder was sintered to each side of expanded silver foil to make the active electrode material. The plates were cut to size, silver wire was spot welded to the plate to serve as plate tabs. The plates were electrochemically anodized in 20% KOH solution to the divalent oxide state. The completed plates were 0.020" thick with a silver density of 1.5 grams of silver per square inch of projected electrode surface.

2. Negative Plate: The negative plates were prepared by applying an active material paste to an expanded silver foil grid. The active material consisted of 85% cadmium metal power (99.9% cadmium less than 15 micron particle size), 10% cadmium oxide, and 5% Ag_2O. Sufficient quantity of a 2% polyvinyl alcohol solution was added to produce a workable paste.

3. Electrolyte: A 40% solution of KOH was used for the electrolyte. A 72 hour soak period was provided for cell equilibration prior to cell testing.

Test Results

Cells E & F: (Previous Report)

These test cells are still on wet stand test to evaluate the self discharge of a duplex plate. These tests are not complete at the date of this report.

Cells G and H:

The performance of these cells over the first few cycles is shown in Figure 5. This graph shows a plot of voltage against the capacity for representative cycles. As is indicated by this plot, the capacity is increasing even with increasing rate of discharge. This type of behavior is characteristic of the type of negative plate used. Previous tests on cells of this type indicate that the capacity would increase to approximately 500 to 600 ampere minutes over the first 100 cycles. After five cycles, a cement joint in the fabricated cell cases developed a severe leak, thus precluding the possibility of further cycling on these cells. Since this type of joint (solvent cement) is inherently weaker than that formed with a catalytic type cement, future cells will be made using molded cell cases from styrene or other suitable material as soon as they become available.

Conclusions:

Certain conclusions have been reached regarding the battery design under development.

1. On the basis of initial tests, the alternate design presented in the Second Quarterly Report is feasible and practical.

2. A glass filament wound outer case that has high strength and gas leak resistance has been made and tested.

FUTURE WORK

Cell Case

It is planned that cell cases be molded of several materials for evaluation purposes. A limited number of cases will be made from polystyrene for initial construction evaluation.

Battery Container

It is planned that two dummy batteries will be assembled for environmental testing of the battery. These will be listed as case numbers 10 and 11. Case Number 10 will be wound on a simulated battery using molded cell cases containing material to simulate cell contents. This assembly will be tested for leakage and moisture permeability. Vibration tests will be conducted and followed by a second leak test to evaluate any possible damage resulting from the exposure to vibration. Any necessary changes will be incorporated into the design and Case Number 11 will be wound and vibration tested to destruction. At this time the final design of the battery assembly will be made.

Electrochemical Design

As soon as molded cell cases become available, a series of cells will be constructed and placed on test. Additional cells will be constructed using any cell cases of new or different materials considered for use.

TABLE I

PERMEABILITY DATA SUMMARY

Rating	H_2O gms/mil/100in^2/day/atm		N_2 cc/mil/100in^2/day/atm		O_2 cc/mil/100in^2/day/atm	
1	Polychlorotrifluoroethylene	1.3	Polyvinylidene chloride	.86	Polyvinylidene chloride	3.0
2	Polyvinylidene chloride	3.0	Polyethyleneterephthalata	1.2	Nylon 6	5.5
3	Polyfluoroethylene propylene	3.9	Nylon	1.7	Polyethyleneterephthalate	5.6
4	Polytetrafluoroethylene	4.4	Polychlorotrifluoro ethylene	9.5	Polychlorotrifluoro-ethylene	30
5	Polyethylene	14	Polystyrene	45	Polyvinylchloride	123
6	Polyethyleneterephthalate	25	Polyfluoroethylene propylene	52	Polyethylene	416
7	Nylon 6	181	Polyethylene	101	Polyfluoroethylene propylene	465
8	Polyvinylchloride	186			Polystyrene	1007
9	Polystyrene	351				
10	Polymethylmethacrylate	738				

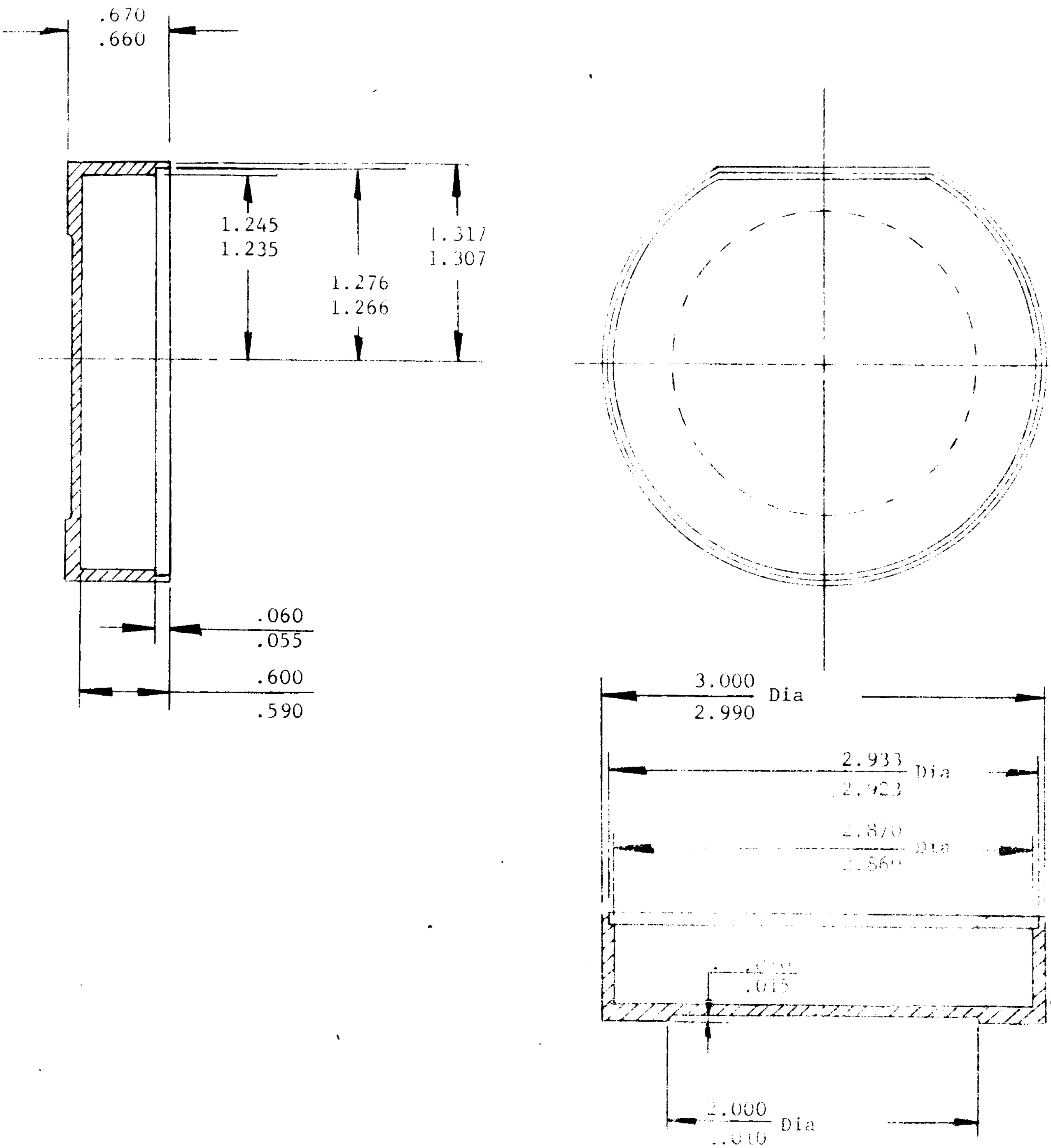


Figure 1. Cell Container

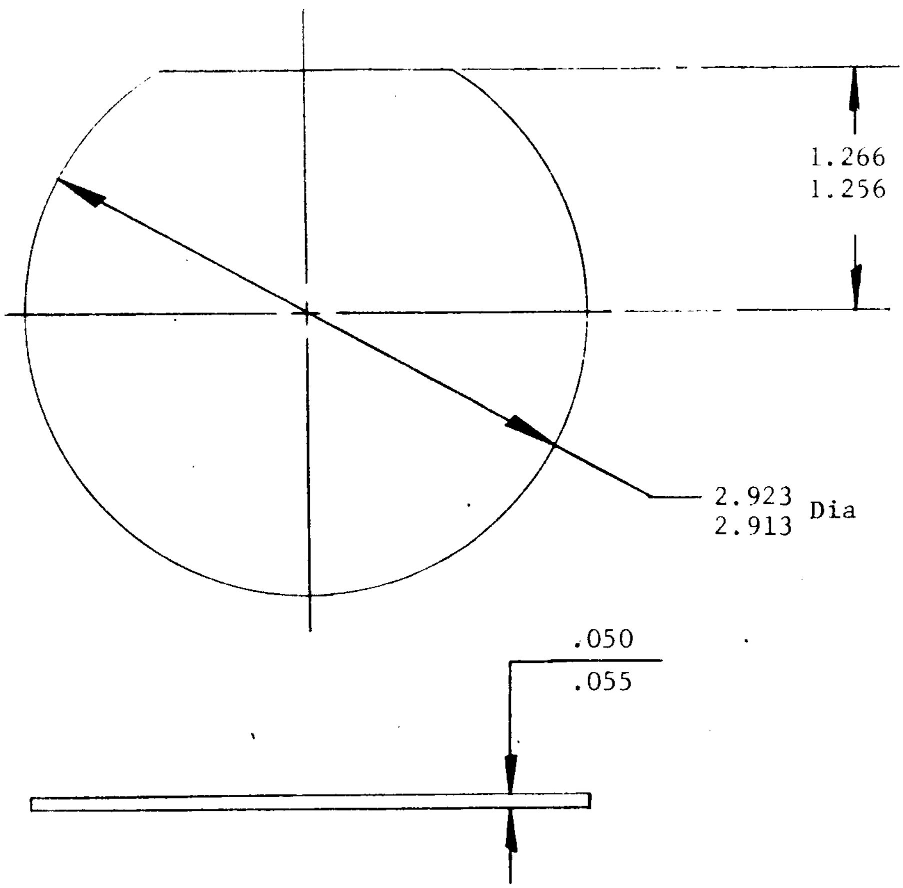


Figure 2. Cover

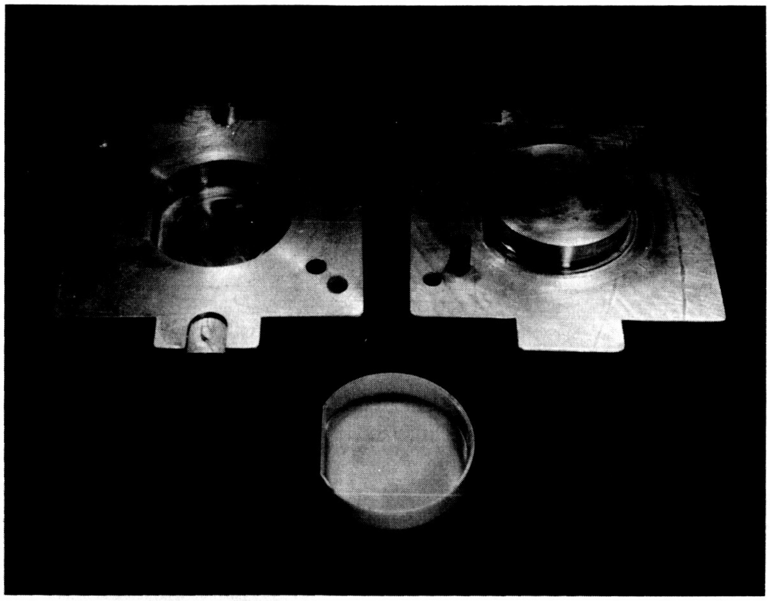


Figure 3. Cell Container Mold
and Molded Container

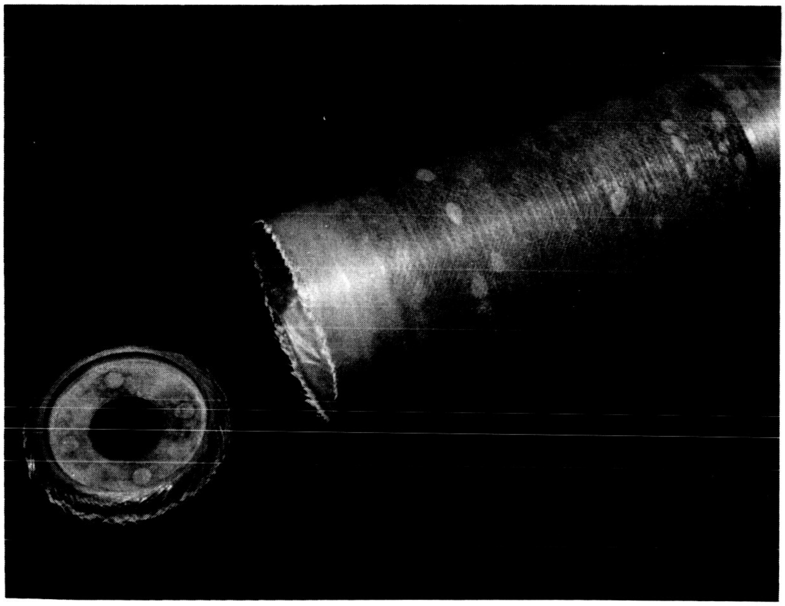
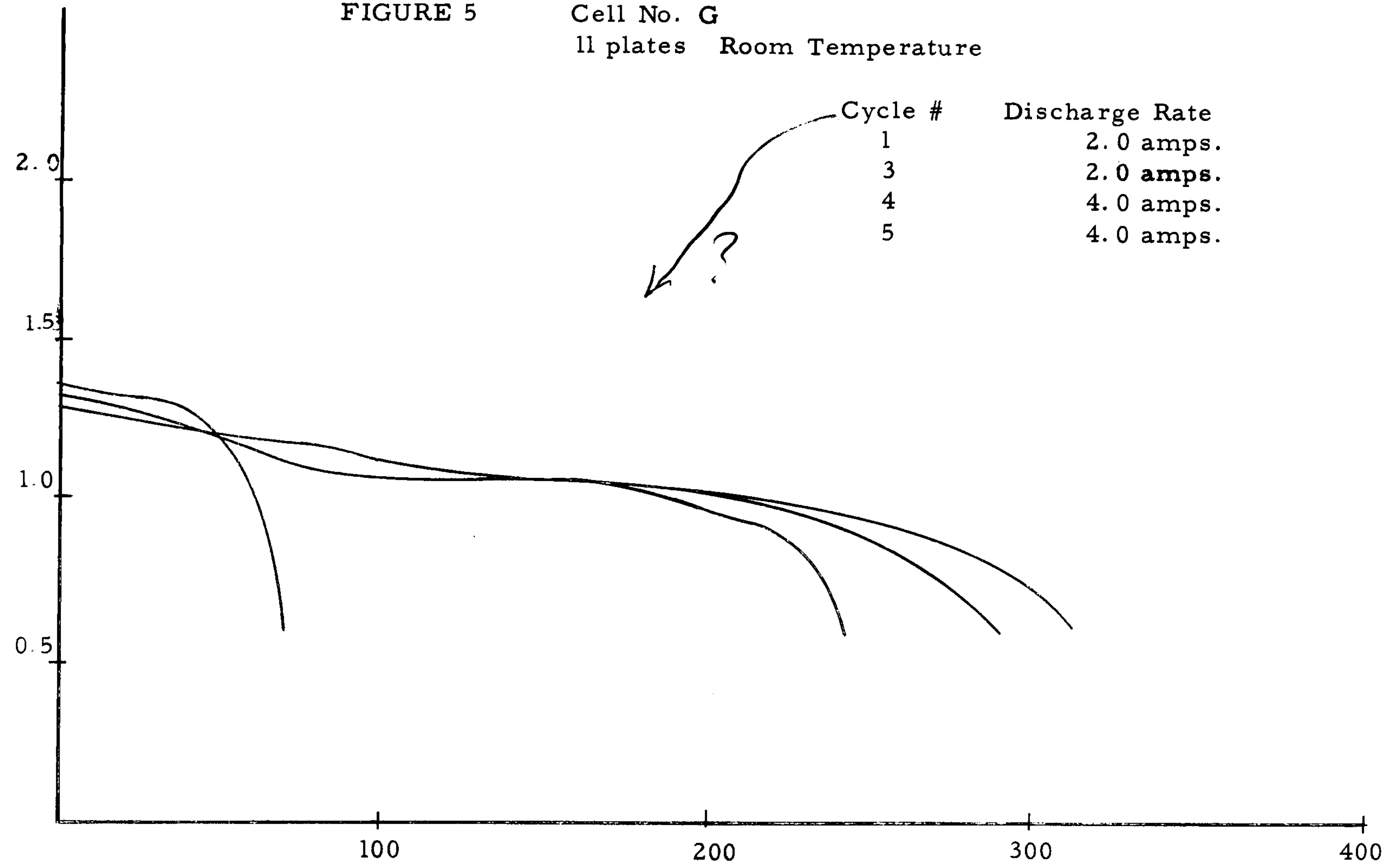


Figure 4. Case No. 9 with Modified
Endplates after Burst Test

FIGURE 5 Cell No. G
11 plates Room Temperature



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POWER SOURCES
DIVISION OF
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3850 OLIVE STREET, DENVER 7, COLORADO, DUDLEY 8-4836

IN REPLY REFER TO:

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August 13, 1962

National Aeronautics and Space Administration
Goddard Space Flight Center
Glendale Road
Greenbelt, Maryland

Attention: Contracting Officer

Subject: Quarterly Technical Progress Report for Third Quarter, Ending 20 May 1962, Silver-Cadmium Battery Development Program
Contract NAS 5-1431

Gentlemen:

Enclosed for your review is one (1) copy of the subject report, which is submitted in accordance with Article VIII.A of the Schedule.

Very truly yours,

W. Burch Winder
Director of Field Engineering

WBW:sp
Distribution: See attached

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National Bureau of Standards
Washington 25, D.C.
Attn: Dr. W. J. Hamer (1)

Power Information Center
Moore School Building
200 South Thirty-Third Street
Philadelphia 4, Pennsylvania

Gulton Industries
Alkaline Battery Division
Metuchen, New Jersey
Attn: Dr. Robert Shair (1)

Gould-National Batteries, Inc.
Engineering and Research Center
2630 University Avenue, SE
Minneapolis 14, Minnesota
Attn: Dr. H. E. Zahn (1)
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Sonotone Corporation
Saw Mill River Road
Elmsford, New York
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Conshohocken, Pennsylvania
Attn: Dr. Eugene Willihganz (1)

General Electric Company
Battery Project
Hudson Falls, New York
Attn: F. R. Flood (1)

General Electric Company
3198 Chestnut St
Philadelphia, Pennsylvania
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Bell Laboratories
Murray Hill, New Jersey
Attn: U. B. Thomas (1)
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S.T.L., 2400 E El Segundo Blvd
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Reliability Control Section
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Denver AF CMO
3800 York Street
Denver 5, Colorado
Attn: RWHOOA